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<p>(54) Title: PRINTING OF OLEFINIC SUBSTRATES COMPRISING A NON-IONIC FLUOROCHEMICAL SURFACTANT</p> <p>(57) Abstract</p> <p>The present invention provides a method of printing a substrate comprising the steps of: providing a substrate selected from the group consisting of (i) a non-woven web comprising fibers of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant and (ii) a microporous film comprising a layer of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant and; image-wise applying ink to said substrate, and the olefinic thermoplastic polymer being a polymer consisting of repeating units derived from alpha olefins having 2 to 4 carbon atoms. It was found that the dispersed fluorochemical surfactant provides improved printability of the microporous film and non-woven web. In connection with the present invention there is also provided a microporous film comprising a layer of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant wherein the olefinic thermoplastic polymer is a polymer consisting of repeating units derived from alpha olefins having 2 to 4 carbon atoms.</p>			

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PRINTING OF OLEFINIC SUBSTRATES COMPRISING A NON-IONIC FLUOROCHEMICAL SURFACTANT

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Field of the Invention

The present invention relates to an improvement in printing of a non-woven web or microporous film of an olefinic thermoplastic polymer. In particular, the improvement involves the addition of a non-ionic fluorochemical surfactant.

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Background of the Invention

Thermoplastic polymers, especially olefinic polymers such as polypropylene, are widely employed to create a variety of substrates, including non-woven fibrous webs and microporous films. In many applications, these substrates need to be provided with printed information such as text and images, including color images. Often, this printed information is provided thereon via ink printing, in particular via inkjet printing. Unfortunately, the aforementioned thermoplastic polymer substrates, when printed in this way, suffer from a number of disadvantages. For example, the appearance of the image may be poor as a result of bleeding of colors and/or coalescence of colors. Furthermore, some inks suffer from slow drying and some may only dry superficially without completely drying throughout within acceptable times. Though these problems are especially noticeable when the ink used is an aqueous based ink, they are not exclusively observed with aqueous based inks. Accordingly, there is a need for a solution that can provide these thermoplastic polymer substrates with improved printability properties.

To modify the surface of thermoplastic olefinic substrates it is known in the art to apply a surface treatment such as corona discharge thereto or to topically apply a hydrophilicity imparting agent as is described in for example GB 1 337 467.

It is further known in the art to modify the surface properties of a thermoplastic polymer by adding a compound during the extrusion of the thermoplastic polymer.

WO 92/18569 and WO 95/01396 describe fluorochemical additives for use in the extrusion of thermoplastic polymers to prepare films and fibers with repellency properties. It is specifically disclosed that films can be prepared with good anti-wetting properties. It is further taught that polypropylene films with the 5 fluorochemical dispersed therein have good antistatic properties.

Furthermore, the addition of one or more surfactants to the melts of thermoplastic polymers to impart hydrophilicity to both the surface and the bulk of the fiber is also taught in the art. U.S. Pat. Nos. 4,857,251 and 4,920,168 (Nohr et al.) describe a method of forming fibers by melt-extrusion of a surface segregatable 10 thermoplastic composition that comprises thermoplastic polymer and siloxane-containing additive having certain moieties. After the fibers are formed, they are heated from 27°C. to 95°C. for a period of time sufficient to increase the amount of additive at the fiber surface. The resulting fibers exhibit increased surface hydrophilicity compared to fibers prepared from the thermoplastic alone.

15 U.S. Pat. No. 5,087,520 (Suzuki et al.) describes fibers useful as surface materials for paper, diapers, sanitary napkins, incontinence products, etc. comprising a polyolefin or polyester having a mixture of a fatty acid diethanolamide, a polyether-modified silicone, a sorbitan fatty acid ester and a metal salt of an alkylsulfonate.

20 US 5,804,625 (Temperante et al.) discloses the addition to the polymer melt of a blend of one or more non-ionic fluorochemical surfactants and one or more non-ionic, non-fluorinated, polyoxyethylene group containing surfactants to impart durable hydrophilicity to the surface of an article extruded from the polymer. Particular articles that can be produced and provided with durable hydrophilicity at 25 the surface include fibers, fabrics and films.

EP 0 516 271 discloses the use of a fluoroaliphatic group containing non-ionic compound in the extrusion of polypropylene fibers to impart durable wettability properties to the fiber's surface. Particularly exemplified compounds are those that have a perfluorinated alkyl group linked to a poly(oxyalkylene) 30 group terminated with a hydroxyl group or a lower alkyl ether.

However, none of the above listed prior art addresses the problem of printability of non-woven webs and microporous films of polyolefinic

thermoplastic polymers. Accordingly, the present invention seeks to improve the printability of such substrates and in particular to reduce color bleeding, color coalescence and/or dry time.

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Summary of Invention

The present invention provides a method of printing a substrate comprising the steps of:

- providing a substrate selected from the group consisting of (i) a non-woven web comprising fibers of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant and (ii) a microporous film comprising a layer of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant and;
- image-wise applying ink to said substrate,

and the olefinic thermoplastic polymer being a polymer consisting of repeating units derived from alpha olefins having 2 to 4 carbon atoms.

Due to the fluorochemical surfactant which is dispersed in the olefinic thermoplastic polymer, improved printability of the microporous film and non-woven web is observed. For example, with the non-woven web, improved drying characteristics are observed, color bleeding is minimized and coalescence is substantially avoided. With the microporous films, less color bleeding and ink coalescence is observed while good drying characteristics are maintained.

It will be understood that in connection with the present invention the use of the term "dispersed therein" denotes merely the presence of the non-ionic fluorochemical surfactant in the thermoplastic polymer without limitation as to where the non-ionic fluorochemical surfactant is located. Thus the non-ionic fluorochemical surfactant may be uniformly dispersed in the bulk of the polymer or a major portion of the non-ionic fluorochemical surfactant may have migrated to the surface of the thermoplastic polymer layer or fiber.

The non-ionic fluorochemical surfactant is typically dispersed in the thermoplastic olefinic polymer by adding it to the polymer melt of the olefinic polymer prior to extruding the fibers of the non-woven web or prior to extruding the precursor of the microporous film.

In connection with the present invention there is also provided a microporous film comprising a layer of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant wherein the olefinic thermoplastic polymer is a polymer consisting of repeating units derived from 5 alpha olefins having 2 to 4 carbon atoms.

Detailed description of the Invention

As used herein, the terms "fiber" and "fibrous" refer to particulate matter, generally thermoplastic resin, wherein the length to diameter ratio of the 10 particulate matter is greater than or equal to about 10. Fiber diameters may range from about 0.5 micron up to at least 1,000 microns. Each fiber may have a variety of cross-sectional geometries, may be solid or hollow, and may be colored by, e.g., incorporating dye or pigment into the polymer melt prior to extrusion.

The non-woven webs of fibers of thermoplastic olefinic polymer for use in 15 this invention include non-woven webs manufactured by any of the commonly known processes for producing non-woven webs. For example, the fibrous non-woven web can be made by spunbonding techniques or melt-blown techniques or combinations of the two. Spunbonded fibers are typically small diameter fibers which are formed by extruding molten thermoplastic polymer as filaments from a 20 plurality of fine, usually circular capillaries of a spinneret with the diameter of the extruded fibers being rapidly reduced. Meltblown fibers are typically formed by extruding the molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into a high velocity, usually heated gas (e.g. air) stream which attenuates the filaments of molten thermoplastic material to reduce their diameter. Thereafter, the meltblown fibers are carried by 25 the high velocity gas stream and are deposited on a collecting surface to form a web of randomly disbursed meltblown fibers. Any of the non-woven webs may be made from a single type of fiber or two or more fibers which differ in the type of thermoplastic olefinic polymer and/or thickness.

30 Further details on the manufacturing method of non-woven webs of this invention may be found in Wente, Superfine Thermoplastic Fibers, 48 INDUS. ENG'G CHEM. 1342(1956), or in WENTE ET AL., MANUFACTURE OF

SUPERFINE ORGANIC FIBERS, (Naval Research Laboratories Report No. 4364, 1954).

The microporous films of the present invention have a structure that enables fluids to flow through them. The effective pore size is at least several times 5 the mean free path of the flowing molecules, namely from several micrometers down to about 100 Angstroms. Such sheets are generally opaque, even when made of transparent material, because the surfaces and the internal structure scatter visible light.

There are several methods known in the art to prepare a microporous film. 10 A preferred method for producing the microporous films of the present invention utilizes the phase separation phenomenon which utilizes either liquid-liquid or solid-liquid phase separation. The method for producing microporous structures using these techniques usually involves melt blending the polymer with a compatible liquid that is miscible with the polymer at the casting or extrusion 15 temperature, forming a shaped article of the melt blend, and cooling the shaped article to a temperature at which the polymer phase separates from the compatible liquid. Microporosity can be imparted to the resultant structure by, for example, (i) orienting the structure in at least one direction; (ii) removing the compatible liquid and then orienting the structure in at least one direction; or (iii) orienting the 20 structure in at least one direction and then removing the compatible liquid. The cooling step for films is usually accomplished by contacting the film with a chill roll. This results in a thin skin being formed on the side of the film which contacts the chill roll, which results in a decrease in the fluid flow through the film. Such methods are described, for example, in U.S. Pat. Nos. 4,247,498 (Castro), 25 4,539,256 (Shipman), 4,726,989 (Mrozinski) and 4,867,881 (Kinzer). Particulate-filled microporous films such as those described in, for example, U.S. Pat. Nos. 4,777,073 (Sheth), 4,861,644 (Young et al.), and 5,176,953 (Jacoby et al.), as well 30 as JP 61-264031 (Mitsubishi Kasei KK), can also be utilized. Microporosity can be imparted to such particulate-filled films by, for example, orienting the film in at least one direction. To produce the microporous film of the present invention having the non-ionic fluorochemical surfactant dispersed therein, the non-ionic fluorochemical surfactant is typically added to the aforementioned melt blend.

In accordance with the present invention, one or more non-ionic fluorochemical surfactants are added to the melt of the olefinic thermoplastic polymer so as to disperse the non-ionic fluorochemical surfactant(s) within the fibers or microporous film produced from the olefinic thermoplastic polymer.

5 Particularly useful non-ionic fluorochemical surfactants include
fluoroaliphatic group-containing nonionic compounds that contain one or more
blocks of water-solubilizing polyoxyalkylene groups in their structures. Generally,
the fluorochemical surfactants useful in the invention include those represented
below by Formula I.

$$10 \quad (R_f)_n - Q - (Z)_m \quad (I)$$

wherein:

each R_f may be the same or different and represents a fluoroaliphatic group having at least 3 and preferably at least 4 fully-fluorinated carbon atoms that may be straight-chained, branched, or, if sufficiently large, cyclic, or any combination

15 thereof. The skeletal chain in the fluoroaliphatic radical can include one or more catenary heteroatoms, such as oxygen, hexavalent sulfur, and trivalent nitrogen atoms bonded only to carbon atoms of the skeletal chain. Fully fluorinated fluoroaliphatic groups are preferred, but hydrogen or chlorine atoms may be present as substituents, as long as no more than one of either atom is present for every two carbon atoms. While R_f can contain a large number of carbon atoms, compounds where R_f has no more than 20 carbon atoms will be adequate and preferred since larger fluoroaliphatic radicals usually represent a less efficient utilization of the fluorine than is possible with shorter fluoroaliphatic radicals.

Fluoroaliphatic radicals containing from about 6 to about 12 carbon atoms are most preferred. Generally, R_f will contain between about 40 and about 78 weight percent fluorine. The terminal portion of the R_f group preferably contains at least four fully fluorinated carbon atoms, e.g., $CF_3CF_2CF_2CF_2\cdot$, and particularly preferred compounds are those in which the R_f group is fully or substantially completely fluorinated, as in the case where R_f is a perfluoroalkyl, e.g., $CF_3(CF_2)_n\cdot$. Suitable R_f groups include, for example, $C_8F_{17}\cdot$, $C_6F_{13}\cdot$, $C_4F_9\cdot$ and $C_{10}F_{21}\cdot$.

Q in Formula I above is a multivalent, generally divalent, linking group, or is a covalent bond, that provides a means to link the group or groups R_f with the

depicted group or groups Z, which is a nonionic, water-solubilizing group; Q can comprise an alkylene group, e.g., $-C_nH_{2n}-$ or $-CH_2CH(OH)CH_2-$; Q can comprise a heteroatom-containing group, e.g., a group such as $-S-$, $-O-$, $-CO-$, $-SO_2-$, or $-N(R)-$ (where R is a hydrogen or a C₁ to C₆ substituted or 5 unsubstituted alkyl group that may comprise a catenary heteroatom such as O, N or S); or Q can comprise a combination of such groups such as would give, for example, $-CON(R)C_nH_{2n}-$, $-SO_2N(R)C_nH_{2n}-$, $-CH_2CH_2SO_2N(R)C_nH_{2n}-$, $-SO_3C_6H_4N(R)C_nH_{2n}-$, $-SO_2N(R)C_jH_{2j}O[CH_2CH(CH_2Cl)O]_gCH_2CH(CH_2Cl)-$ (n' = 1 to 6; g = 1 to 10), 10 $-SO_2N(CH_3)C_2H_4OCH_2CH(OH)CH_2-$, $-SO_2N(C_2H_5)C_2H_4OCH_2CH(OH)CH_2-$, $-SO_2N(H)CH_2CH(OH)CH_2NHCH(CH_3)CH_2-$, $-(CH_2)_2S(CH_2)_2-$, and $-(CH_2)_4SCH(CH_3)CH_2-$; each Z in Formula I above may be the same or different and represents a nonionic, 15 water-solubilizing group comprising a poly(oxyalkylene) group, (OR')_x, where R' is an alkylene group having from 2 to about 4 carbon atoms, such as $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH(CH_3)CH_2-$, and $-CH(CH_3)CH(CH_3)-$, and x is a number between about 6 and about 20; Z preferably contains a poly(oxyethylene) group. The oxyalkylene units in said poly(oxyalkylene) can be the same, such as in 20 poly(oxypropylene) or poly(oxyethylene), or can be present as a mixture, such as in a heteric straight or branched chain of randomly distributed oxyethylene and oxypropylene units, i.e., poly(oxyethylene-co-oxypropylene), or as in straight or branched chain blocks of oxypropylene units. The poly(oxyalkylene) chain can be interrupted by or include one or more catenary linkages, providing such linkages 25 do not substantially alter the water-solubilizing character of the poly(oxyalkylene) chain. The Z group may be terminated for example with a hydroxyl, lower alkyl ether, alkaryl ether, or fluoroalkyl ether; and n and m independently represent a number from 1 to 6. Preferably, n and m are 1.

A preferred subclass of the non-ionic fluorocchemical compounds according 30 to formula (I) for use in this invention corresponds to formula (II):



wherein R_f has the meaning as described above; L either is a divalent linking group

such as, for example, one of the divalent linking groups mentioned above for Q or is a covalent bond; G is a water solubilizing poly(oxyalkylene) group; X is oxygen or NR, with R representing hydrogen or an alkyl or aryl group; and T is hydrogen or an organic group, preferably an organic group having not more than 6 carbon atoms.

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Specific examples of non-ionic fluorochemical surfactants for use in the invention include:

- C₈F₁₇SO₂N(C₂H₅)CH₂CH₂(OCH₂CH₂)_{7.2}OCH₃
- C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)_{7.2}OCH₃
- 10 C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)_{8.5}OC₄H₉
- C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)_{8.5}OC₆H₁₃
- C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)₁₀OC₈H₁₇
- C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)₁₀OC₁₀H₂₁
- C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)_{9.5}OC₆H₅
- 15 C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)_{9.5}OC₁₄H₂₉
- C₈F₁₇SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)₁₀OC₆H₄-C₈H₁₇
- C₈F₁₇SO₂N(C₂H₅)CH₂CH₂(OCH₂CH₂)₉OCH₂CH₃
- C₇F₁₅SO₂N(CH₃)CH₂CH₂(OCH₂CH₂)₇(OCH₂CH(CH₃))₄OH
- C₈F₁₇SO₂N(C₂H₅)CH₂CH₂NHCH₂CH₂(OCH₂CH₂)₉NHC(O)-CH₃
- 20 F(CF₂CF₂)_nCH₂CH₂O(CH₂CH₂O)_xH

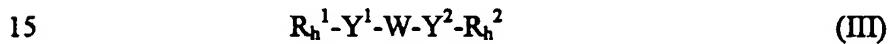
wherein the above formula represents a mixture of compounds wherein n has a value of 2 to 6 and the average is 4 and x is about 14;

Fluoroaliphatic group-containing non-ionic fluorochemical surfactants, including those depicted supra by Formula I and II, may be prepared using known methods including those methods described in U.S. Pat. No. 2,915,554 (Albrecht et al.). The Albrecht patent discloses the preparation of fluoroaliphatic group-containing nonionic compounds from active hydrogen-containing fluorochemical intermediates, such as fluoroaliphatic alcohols, acids, and sulfonamides by reaction of the intermediates with, for example, ethylene oxide.

30 Analogous compounds may be prepared by treating the fluorochemical intermediate with propylene oxide. The fluoroaliphatic oligomers disclosed in U.S. Pat. No. 3,787,351 (Olson), and certain fluorinated alcohol-ethylene oxide

condensates described in U.S. Pat. No. 2,723,999 (Cowen et al.), whose descriptions are incorporated herein by reference, are also considered useful. Fluoroaliphatic group-containing nonionic surfactants containing hydrophobic long chain hydrocarbon groups may be prepared by reacting a fluoroaliphatic epoxide, 5 with, for example, an ethoxylated alkylphenol or alcohol, respectively, in the presence of BF_3 etherate. They may also be prepared by first converting the ethoxylated alkylphenol or alcohol to a chloride by reaction with thionyl chloride, then reacting the resulting chloride with a fluoroaliphatic sulfonamide containing an active hydrogen, in the presence of sodium carbonate and potassium iodide.

10 In accordance with a particular embodiment of the present invention, there may further be dispersed a non-fluorochemical non-ionic polyoxyalkylene surfactant (hereinafter hydrocarbon surfactant) in the thermoplastic olefinic polymer. Preferably, the hydrocarbon surfactant corresponds to the following formula:



wherein:

W represents a polyoxyalkylene group, preferably a polyoxyethylene group;

20 Y^1 and Y^2 independently represent an oxygen or sulfur atom or a group of the formula -CO-, -COO-, -NH-, -CONH-, or -N(R)-, where R is an alkyl group or an aryl group;

25 R_h^1 represents an alkyl or an aryl group, or a combination thereof, that may be substituted or unsubstituted and that contains from 2 to about 20 carbon atoms whose skeletal chain may be straight-chained, branched, or, if sufficiently large, cyclic, or any combination thereof, the skeletal chain can also optionally include one or more catenary heteroatoms (such as oxygen, hexavalent sulfur, and trivalent nitrogen atoms) bonded to the carbon atoms of the skeletal chain, and

30 R_h^2 represents a hydrogen atom or is an alkyl or an aryl group, or a combination thereof, that may be substituted or unsubstituted and that contains from 2 to about 20 carbon atoms whose skeletal chain may be straight-chained, branched, or, if sufficiently large, cyclic, or any combination thereof; the skeletal chain can also optionally include one or more catenary heteroatoms such as

oxygen, hexavalent sulfur, and trivalent nitrogen atoms bonded to the carbon atoms of the skeletal chain.

The variable W in the hydrocarbon surfactants according to the above formula III is a polyoxyalkylene group (OR')_s, where R' is an alkylene group having from 2 to about 4 carbon atoms, such as --CH₂CH₂--, --CH₂CH₂CH₂--, --CH(CH₃)CH₂--, and --CH(CH₃)CH(CH₃)--, and s is a number such that the weight percent of oxyalkylene units in the hydrocarbon surfactant is between 20 and 80 percent and more preferably between 40 and 70 weight percent. The oxyalkylene units in the poly(oxyalkylene) group can be the same, such as in poly(oxypropylene) or poly(oxyethylene), or present as a mixture, such as in a heteric straight or branched chain of randomly distributed oxyethylene and oxypropylene units i.e., poly(oxyethylene-co-oxypropylene), or as in a straight or branched chain blocks of oxypropylene units.

Representative hydrocarbon surfactants according to Formula III above include ethoxylated alkylphenols (such as the TRITON™ TX, IGEPAL™ CA and IGEPAL™ CO series, commercially available from Union Carbide Corp. and Rhone-Poulenc Corp. respectively), ethoxylated dialkylphenols (such as the IGEPAL™ DM series, also commercially available from Rhone-Poulenc Corp.), ethoxylated fatty alcohols (such as the TERGITOL™ series, commercially available from Union Carbide Corp.) and polyoxyethylene fatty acid mono-esters and diesters (such as the MAPEG™ MO and MAPEG™ DO series, commercially available from PPG Industries, Inc.).

When one or more non-ionic fluorochemical surfactants are blended with one or more hydrocarbon surfactants the weight ratio of non-ionic fluorochemical surfactant(s) to hydrocarbon surfactants(s) is typically from 9:1 to 4:6, preferably from 9:1 to 1:1, more preferably from 9:1 to 6:4.

The olefinic thermoplastic polymer used to produce the non-woven web or microporous film of the present invention is a poly(alpha)olefin consisting of repeating units derived from mono-1-olefins (alpha olefins) having 2 to 4 carbon atoms. The monomers that can be employed to produce the thermoplastic olefinic polymer for use in this invention include ethylene, propylene and butene-1, alone, or in admixture, or in sequential polymerization systems.

Examples of suitable polymers include polyethylene, the presently preferred polypropylene, propylene/ethylene copolymers, polybutylene and blends thereof. Processes for preparing these polymers are well known, and the invention is not limited to a polymer made with a particular catalyst or process.

5 The non-ionic fluorochemical surfactant or blend thereof with a hydrocarbon surfactant is typically added to the melt of the olefinic polymer prior to extrusion and is typically added in an amount of at least 0.2% by weight based on the weight of the thermoplastic olefinic polymer and more preferably in an amount of at least 0.5% by weight. The maximum amount of the non-ionic 10 fluorocultural surfactant is not critical; however, it is preferred not to use excessive amounts so as to not impair the mechanical properties of the microporous film or the fibers of the non-woven web. Generally, the amount of non-ionic fluorochemical surfactant or blend with a hydrocarbon surfactant is between 0.3% by weight and 10% by weight, more preferably between 0.5% by 15 weight and 6% by weight based on the weight of the thermoplastic olefinic polymer.

When nonwoven webs or microporous films are prepared containing less than 2.0 weight percent of the non-ionic fluorochemical surfactant or blend thereof with the hydrocarbon surfactant, the non-ionic fluorochemical surfactant or blend 20 is conveniently incorporated into the polymer by tumble blending the non-ionic fluorochemical surfactant or blend with polymer pellets prior to extrusion or by metering liquid non-ionic fluorochemical surfactant or blend into the extruder hopper along with the polymer pellets during extrusion. When greater than about 2.0 weight percent of non-ionic fluorochemical surfactant or blend is used, it is 25 preferable to inject the non-ionic fluorochemical surfactant or blend into the molten polymer stream under high pressure either in the extruder barrel or immediately as the melt stream exits the extruder and before it enters the extrusion die. For convenience, a "master batch" or superconcentrate of non-ionic fluorochemical surfactant or blend thereof with a hydrocarbon surfactant in 30 thermoplastic olefinic polymer can be made (e.g., thermoplastic olefinic polymer containing 5-30 weight percent of the non-ionic fluorochemical surfactant or blend

which was melted and extruded into pellets) and added to the remaining thermoplastic olefinic polymer before the extrusion process.

In accordance with the method of the present invention, the non-woven web or the microporous film is provided in an image-wise fashion with ink. By the 5 term "image-wise applying" in connection with the invention is meant that an ink pattern is applied representing information such as signs, graphs, drawings, images, text or any combination thereof. The ink that is applied to the non-woven web or the microporous film can be any type of ink commonly used in the art. For example, the ink can be aqueous based as well as solvent based. Further, the ink 10 may be based on dyes that are dissolved in the ink or that are present in the ink as finely dispersed pigments. The image-wise application of the ink on the substrates of the invention conveniently proceeds by means of an inkjet printer. Commercially available inkjet printers that can be used in connection with the 15 invention include for example the Hewlett Packard printers HP 855 desk jet, HP 870 desk jet, HP 2000c desk jet, HP 2500 Design Jet and the Encad printers Novajet IV and Novajet Pro.

The invention is further illustrated by means of the following examples without the intention to limit the invention thereto.

20 EXAMPLES

All percentages shown in the examples and test methods which follow are by weight unless otherwise specified.

GLOSSARY

25 Fluorochemical Surfactants

FC-1: 3M™ FC-1802 Protective Chemical, a hydrophilic melt additive for nonwovens, available from 3M Co., St. Paul, Minnesota.

FC-2: This fluorochemical is the reaction product of MeFOSA ($C_8F_{17}SO_2NH_2$) with GENAPOL™ 26-L-80, prepared as described for 30 Fluoroaliphatic Group-containing Nonionic Compound F-21 in U.S. Pat. No. 5,804,625. GENAPOL™ 26-L-80 is nominally $C_{12-16}H_{25-33}(OCH_2CH_2)_{9.5}OH$, available from Clariant Corp., Charlotte, North Carolina.

FC-3: This fluorochemical is the reaction product of MeFOSA with ALFONIC™ 6-8.5, prepared as described for Fluoroaliphatic Group-containing Nonionic Compound F-21 in U.S. Pat. No. 5,804,625, except that an equimolar amount of ALFONIC™ 6-8.5 was substituted for the GENAPOL™ 26-L-80.

5 **ALFONIC™ 6-8.5** is nominally $C_6H_{13}(OCH_2CH_2)_{8.5}OH$, available from Condea Vista Chemical Co., Houston, Texas.

FC-4: This fluorochemical is the reaction product of MeFOSA with CARBOWAX™ 350, prepared as described for Fluoroaliphatic Group-containing Nonionic Compound F-18 in U.S. Pat. No. 5,804,625 at col. 12, except that an 10 equimolar amount of CARBOWAX™ 350 was substituted for TRITON™ X-100. CARBOWAX™ 350 is nominally polyethylene glycol 350 monomethyl ether, available from Union Carbide Corp., Danbury, Connecticut.

Non-Fluorochemical Surfactants

15 **HC-1:** GENAPOL™ UD080 surfactant, an oxo alcohol polyglycol ether, available from Clariant Corp.

HC-2: TRITON™ X-100 surfactant, ethoxylated (9.5) octylphenol, available from Union Carbide Corp, Danbury, Connecticut.

HC-3: NUWET™ 500 silicone surfactant, available from OSI Specialties, 20 Inc., Danbury, Connecticut.

Thermoplastic Polymers

PP3505: ESCORENET™ PP3505 polypropylene, having a 400 melt index flow rate, available from Exxon Chemical Co., Baytown, Texas.

25 **P(EO)6806:** ASPUN™ 6806 poly(ethylene/octene), having a melt index of 105 g/10 min (as measured by Test Method ASTM D-1238) and having a peak melting point of 124.8°C, available from Dow Chemical Co., Midland, Michigan.

SD45: polypropylene, having a melt index of 0.6 dg/min (available from Union Carbide Corp.)

Miscellaneous

MILLAD™ 3905 nucleating agent - available from Milliken Chemical Co., New York, New York.

5 **USP #31 mineral oil** - available from Amoco Petroleum Products, Oak Brook, Illinois.

TEST METHODSMelt-Blown Extrusion Procedure

The melt-blown extrusion procedure used was the same as described in 10 U.S. Pat. 5,300,357, column 10, which is herein incorporated by reference. The extruder used was a Brabender 42 mm conical twin screw extruder, with maximum extrusion temperature of 270-280°C and distance to the collector of 12 inches (30 cm). Fluorochemical surfactant (with optional hydrocarbon surfactant) and thermoplastic polymer mixtures were mixed by blending the surfactant(s) and 15 thermoplastic polymer in a paperboard container using a mixer head affixed to a hand drill for about one minute until a visually homogeneous mixture was obtained. The process condition for each mixture was the same, including the melt blowing die construction used to blow the microfiber web. The basis weight of the resulting web, unless otherwise stated, was $100 \pm 5 \text{ g/m}^2$ (GSM), and the desired 20 diameter of the microfibers was 5-18 micrometers. Unless otherwise stated, the extrusion temperature was 270-280°C, the primary air temperature was 210°C, the pressure was 124 kPa (18 psi), with a 0.076 cm air gap width, and the polymer throughput rate was about 180 g/hr/cm.

25 Microporous Film Preparation Procedure

Control Microporous Film (No Additive) - About 64.9% 5D45 polypropylene and about 0.1% **MILLAD™ 3905** nucleating agent were melt mixed with 35% USP #31 mineral oil on a 40 mm twin screw extruder operated at a throughput rate of 11.8 kg/hour and at a decreasing temperature profile of 270°C 30 to 216°C. The melt mix was extruded through a 38 cm x 0.38 mm sheeting die and then was cast onto a patterned casting wheel maintained at 56°C. The resulting film was first stretched at a ratio of 1.25:1 at 52°C in the length direction, then

stretched at a ratio of 1.65:1 at 107°C in the transverse direction, and finally heat set at a temperature of 132°C for 10 seconds. The resulting microporous film had an average pore size of 0.60 microns and thickness of 0.18 mm.

Microporous Film Made with Fluorochemical Surfactant Polymer

5 **Melt Additive** - Essentially the same process and raw materials were employed as described in the preparation of the control microporous film, except this time 1.2% of fluorochemical surfactant FC-4 was added to the polypropylene/nucleating agent/oil blend prior to extrusion. In addition, the nucleator concentration was increased from 0.1% to 0.22%. The resulting microporous film had an average
10 pore size of 0.17 microns and thickness of 0.18 mm.

Microporous Film Made with Hydrocarbon Surfactant Polymer Melt

Additive - Essentially the same process and raw materials were employed as described in the preparation of the control microporous film, except this time 0.6% of hydrocarbon surfactant HC-2 was added to the polypropylene/nucleating
15 agent/oil blend prior to extrusion. In addition, the nucleating agent concentration was increased from 0.1% to 0.22%. The resulting microporous film had an average pore size of 0.17 microns and thickness of 0.18 mm.

Microporous Film with a Blend of Fluorochemical and Hydrocarbon Surfactant Polymer Melt Additives - Essentially the same process and raw

20 materials were employed as described in the preparation of the control microporous film, except this time 0.5% each of fluorochemical surfactant FC-4 and hydrocarbon surfactant HC-2 were added to the polypropylene/nucleating agent/oil blend prior to extrusion. In addition, the nucleating agent concentration was increased from 0.1% to 0.20%. The resulting microporous film had an
25 average pore size of 0.95 microns and thickness of 0.18 mm.

Printing of Substrates

Substrates (nonwovens webs or microporous films) were each attached to a paper backing and then were passed through a test printer. Each substrate was
30 given a three-color print with symmetrically overlapping, same-sized solid circles of yellow, magenta and cyan ink. In this way, separate inked areas were provided for yellow, magenta and cyan (primary colors), overlapping print areas for the two-

color combinations of yellow with magenta, yellow with cyan and magenta with cyan (secondary colors), and a doubly overlapping print area for the three-color combination of yellow, magenta and cyan (tertiary color – theoretically black). The printed substrate was then observed or tested for bleed, coalescence and ink 5 dry time (surface and total), according to the test procedures described below.

Bleed

Bleed is a measurement of the degree of ink feathering/bleeding/flooding noted on the surface of the printed substrate. Feathering and bleeding are terms 10 used to describe the spreading of one ink color onto another. Flooding is the term used to describe the situation where the printed substrate is unable to hold the amount of ink being jetted, thus causing running or spilling of one color onto another. All of these terms describing ink bleeding have been taken into account in the following 4-point rating scale:

15 1 - GOOD - no bleeding, feathering or flooding noted (inks stays in original printed location)

2 2 - FAIR - secondary color feathering or bleed (ink boundaries become indistinct)

3 3 - POOR - secondary color flooding (ink shows some running over 20 surface)

4 4 - SEVERE - primary bleeding and secondary flooding (severe ink bleeding and running)

Uniformity

25 Uniformity is a measurement of the ink density on the printed substrate. It is desirable that the ink uniformly wet the substrate and not exhibit any significant degree of coalescence, beading, mottling and/or mud-cracking. Coalescence and beading are terms used to describe the situation where the ink does not properly wet the media, causing the ink to pool together in bead-like forms. Mud-cracking 30 is a term to describe when the ink exhibits cracking or splitting from the substrate surface, with substrate showing between the ink cracks. Mud-cracking is often a result of receptor or ink film shrinkage or possibly pigment agglomeration during

drying. Mottling is a term used to describe the appearance of a non-uniform blotchy image, often caused by receptor absorbency variations across the printed areas. Factors adversely affecting ink uniformity include receptor coating thickness variations and contamination of the receptor surface. Common contaminants 5 preventing proper absorbency of the ink onto the substrate surface include silicones and oils. All of these terms describing ink uniformity on the substrate have been taken into account in the following 4-point rating scale:

- 1 - GOOD - no coalescing of ink noted
- 2 - FAIR - mud cracking of ink noted
- 10 3 - POOR - mottling of ink noted
- 4 - SEVERE - beading and coalescing of ink noted

Surface Dry Time

Surface dry time represents the amount of time required for the ink surface 15 of the printed substrate to become dry to the touch. It is desirable that the surface dry time be as short as possible.

Total Dry Time

Total dry time represents the amount of time for the ink on the printed 20 substrate to become totally dry, i.e., not easily smudged by finger touch or by rubbing together adjacent printed substrate layers. It is desired that the total dry time be as short as possible.

Examples 1-3 and Comparative Examples C1-C5

25 Using the Melt Blown Extrusion Procedure, 100 g/m² nonwoven webs were formed from meltblown PP3505 polypropylene fibers containing the following polymer melt additive(s):

Example 1: 1.0% FC-1

Example 2: 1.0% FC-2 + 1.0% HC-2

30 Example 3: 0.75% FC-3 + 0.75% HC-1

Comp. Ex. C1: none (control)

Comp. Ex. C2: 1.25% HC-2

Comp. Ex. C3: 6% HC-2

Comp. Ex. C4: 1.25% HC-3

Comp. Ex. C5: 6% HC-3 (silicone surfactant)

The nonwoven webs were fed into a Hewlett Packard HP 855 DeskJet

5 Printer (available from Hewlett Packard Corp., Palo Alto, California) which produces 600 dpi black text and 300 dpi color images. This printer uses two replaceable cartridges from Hewlett Packard, containing dye inks, each containing inks having a relatively high surface tension: an HP51645A cartridge containing black ink and an HP51641A cartridge containing three separate inks, cyan, magenta and yellow. The quality of ink printing was rated according to Bleed, Uniformity, Surface Dry Time and Total Dry Time. Results from these evaluations are presented in TABLE 1.

10

TABLE 1

<u>Ex.</u>	<u>FC, %</u>	<u>HC, %</u>	<u>Basis Weight</u>	<u>Bleed</u>	<u>Uni-formity</u>	<u>Surface Dry Tm.</u>	<u>Total Dry Tm.</u>
1	FC-1, 1%	—	100 GSM	1.0	1.0	12 min	37 min
3	FC-2, 1%	HC-2, 1%	100 GSM	1.3	1.0	17 min	19 hr
2	FC-3, 0.75%	HC-1, 0.75%	100 GSM	1.0	1.0	2 min	2 min
C1	—	—	100 GSM	1.5	1.0	> 24 hr	> 24 hr
C2	—	HC-2, 1.25%	40 GSM	1.3	1.0	9 min	> 24 hr
C3	—	HC-2, 6%	40 GSM	1.5	1.0	20 min	> 24 hr
C4	—	HC-3, 1.25%	40 GSM	1.5	1.0	200	> 24 hr
C5	—	HC-3, 6%	40 GSM	1.5	1.0	5	> 24 hr

15

The data in TABLE 1 show that, with the HP 855 printer, a much faster ink dry time, especially total dry time, resulted when a fluorochemical surfactant or fluorochemical/hydrocarbon surfactant blend was incorporated in the polypropylene fibers, when compared to incorporating a hydrocarbon surfactant, a silicone surfactant, or no surfactant at all.

20

Comparative Examples C6-C8

Using the Melt Blown Extrusion Procedure, nonwoven webs having a basis weight of 100 g/m² were formed from meltblown P(EO)6806 poly(ethylene/octene) fibers containing the following polymer melt additive(s):

5 Comp. Ex. C6: 1.0% FC-1

Comp. Ex. C7: 0.5% FC-3 + 0.5% HC-1

Comp. Ex. C8: none (control)

The nonwoven webs were fed into a Hewlett Packard HP 855 DeskJet Printer containing the same ink cartridges as previously described, and quality of 10 ink printing on each web was rated according to Bleed, Uniformity, Surface Dry Time and Total Dry Time. Results from these evaluations are presented in TABLE 2.

TABLE 2

<u>Ex.</u>	<u>FC, %</u>	<u>HC, %</u>	<u>Bleed</u>	<u>Uni-formity</u>	<u>Surface Dry Tm.</u>	<u>Total Dry Tm.</u>
C6	FC-1, 1%	—	1.0	1.0	9 min	> 24 hr
C7	FC-3, 0.5%	HC-1, 0.5%	1.0	1.0	29 min	> 24 hr
C8	—	—	1.5	1.0	27 min	> 24 hr

15

The data in TABLE 2 show that when the HP 855 printer was used to apply ink onto a web made of poly(ethylene/octene) fibers instead of polypropylene fibers, no consistent improvement in bleed, uniformity or dry time resulted when a fluorochemical surfactant was incorporated as a polymer melt additive, either used 20 alone or blended with a hydrocarbon surfactant.

Examples 4-5 and Comparative Examples C9-C11

Using the Melt Blown Extrusion Procedure, 100 g/m² nonwoven webs were formed from either meltblown PP3505 polypropylene fibers or meltblown 25 PEO6806 poly(ethylene/octene) fibers containing the following polymer melt additive(s):

Example 4: PP3505 + 1.0% FC-1

Example 5: PP3505 + 0.75% FC-3 + 0.75% HC-1

Comp. Ex. C9: PP3505 alone

Comp. Ex. C10: P(EO)6806 + 1% FC-1

Comp. Ex. C11: P(EO)6806 alone

5 This time, the nonwoven webs were fed into a Hewlett Packard HP 2000C Professional Series Color Printer (available from Hewlett Packard Corp.), which produces 600 dpi black print quality and 300 dpi color print quality. This printer uses four replaceable cartridges: C4841A Cyan, C4843A Magenta, C4842A Yellow and C4844A Black, available from Hewlett Packard Corp., containing dye-type inks, having a relatively low surface tension (20 picoLiter drops). The quality of ink printing was rated according to Bleed, Uniformity, Surface Dry Time and Total Dry Time. Results from these evaluations are presented in TABLE 3.

10

TABLE 3

<u>Ex.</u>	<u>FC, %</u>	<u>HC, %</u>	<u>Polymer</u>	<u>Bleed</u>	<u>Uni-formity</u>	<u>Surface Dry Tm.</u>	<u>Total Dry Tm.</u>
4	FC-1, 1%	—	PP- 3505	1.0	1.0	4.5 min	80 min
5	FC-3, 0.75%	HC-1, 0.75%	PP- 3505	1.0	1.0	14 min	135 min
C9	—	—	PP- 3505	1.0	1.0	80 min	> 24 hr
C10	FC-1, 1%	—	P(EO)- 6806	1.0	1.0	35 min	> 24 hr
C11	—	—	P(EO)- 6806	1.0	1.0	32 min	270 min

15

The data in TABLE 3 show that when the HP 2000C printer was used to apply ink to the polypropylene nonwoven webs, a much faster ink drying time, especially for the ink to totally dry, resulted when the fluorochemical surfactant or fluorochemical/hydrocarbon surfactant blend was incorporated in the
20 polypropylene fibers, when compared to incorporating no surfactant at all. No significant improvement in print quality or dry time was noted when the same fluorochemical surfactant or fluorochemical/hydrocarbon surfactant blend was incorporated in the poly(ethylene/octene) fibers.

Examples 6-7 and Comparative Examples C12-C14

Using the Melt Blown Extrusion Procedure, 100 g/m² nonwoven webs were formed from either meltblown PP3505 polypropylene fibers or meltblown PEO6806 poly(ethylene/octene) fibers containing the following polymer melt 5 additive(s):

Example 6: PP3505 + 1.0% FC-1

Example 7: PP3505 + 0.75% FC-3 + 0.75% HC-1

Comp. Ex. C12: PP3505 alone

Comp. Ex. C13: P(EO)6806 + 1% FC-1

10 Comp. Ex. C14: P(EO)6806 alone

This time, the nonwoven webs were fed into a Hewlett Packard HP DesignJet 2500CP Printer, (available from Hewlett Packard Corp.), which produces 600 dpi color images. This printer uses four replaceable cartridges available from Hewlett Packard Corp. containing DesignJet CP Ink System UV 15 pigment-type inks C1893A Cyan, C1894A Magenta, C1895A Yellow and C1892A Black, each ink having a relatively low surface tension (20 picoLiter drops in eight passes). The quality of ink printing was rated according to Bleed, Uniformity, Surface Dry Time and Total Dry Time. Results from these evaluations are presented in TABLE 4.

20

TABLE 4

<u>Ex.</u>	<u>FC. %</u>	<u>HC. %</u>	<u>Poly- mer</u>	<u>Bleed</u>	<u>Uni- formity</u>	<u>Surface Dry Tm.</u>	<u>Total Dry Tm.</u>
6	FC-1, 1%	—	PP-3505	1.5	1.0	1.5 min	2.5 min
7	FC-3, 0.75%	HC-1, 0.75%	PP-3505	1.5	1.0	1.75 min	2.5 min
C12	—	—	PP-3505	1.5	1.0	2 min	4 min
C13	FC-1, 1%	—	P(EO)- 6806	1.5	1.0	1.5 min	2.5 min
C14	—	—	P(EO)- 6806	1.5	1.0	1 min	1.5 min

The data in TABLE 4 show that, using the HP 2500CP printer to apply inks to polypropylene nonwoven webs, a faster surface and total dry time resulted when 25 a fluorochemical surfactant or fluorochemical/hydrocarbon surfactant blend was

incorporated in the polypropylene fibers, as compared to when no surfactant was incorporated. Dry times were somewhat lengthened when the same fluorochemical surfactant or fluorochemical/hydrocarbon surfactant blend was incorporated in the poly(ethylene/octene) fibers.

5

Examples 8-9 and Comparative Example C15

Using the Melt Blown Extrusion Procedure, 100 g/m² nonwoven webs were formed from meltblown PP3505 polypropylene fibers containing the following polymer melt additive(s):

10 Example 8: PP3505 + 1.0% FC-1

Example 9: PP3505 + 0.75% FC-3 + 0.75% HC-1

Comp. Ex. C15: PP3505 alone

This time, the nonwoven webs were fed into a wide format ENCAD NOVAJET™ 4 Printer (available from ENCAD Corp., San Diego, California) which produces 300 dpi black and color images. This printer uses four replaceable cartridges available from ENCAD Corp. containing 3M Thermal InkJet pigment-type inks: 8551 Cyan, 8553 Magenta, 8552 Yellow and 8554 Black, each ink having a relatively high surface tension (140 pl drops). The quality of ink printing was rated according to Bleed, Uniformity, Surface Dry Time and Total Dry Time.

20 Results from these evaluations are presented in TABLE 5.

TABLE 5

Ex.	FC, %	HC, %	Bleed	Uni-formity	Surface Dry Tm.	Total Dry Tm.
8	FC-1, 1%	—	2.0	1.0	3 min	8 min
9	FC-3, 0.75%	HC-1, 0.75%	2.0	1.0	8 min	14 min
C15	—	—	1.5	1.0	20 min	between 4 and 18 hrs

The data in TABLE 5 show that, using an ENCAD NOVAJET 4 printer to apply ink to nonwoven webs, a considerably faster time for the ink to surface dry and become totally dry resulted when a fluorochemical surfactant or

fluorochemical/hydrocarbon surfactant blend was incorporated in the polypropylene fibers, as compared to when no surfactant was incorporated.

Examples 10-11 and Comparative Examples C16-C17

5 Using the Microporous Film Preparation Procedure, microporous films were formed from 5D45 polypropylene containing the following polymer melt additive(s):

Example 10: 5D45 + 1.2% FC-4

Example 11: 5D45 + 0.5% FC-4 + 0.5% HC-2

10 Comp. Ex. C16: 5D45 + 0.6% HC-2

Comp. Ex. C17: 5D45 alone

The microporous films were printed with a Hewlett Packard HP DesignJet 2500CP Printer having the same ink cartridges as previously described. The quality of ink printing was rated according to Bleed, Uniformity, Surface Dry Time 15 and Total Dry Time. Results from these evaluations are presented in TABLE 6.

TABLE 6

<u>Ex.</u>	<u>FC, %</u>	<u>HC, %</u>	<u>Bleed</u>	<u>Uni-formity</u>	<u>Surf. Dry Tm.</u>	<u>Total Dry Tm.</u>
10	FC-4, 1.2%	—	1.5	1.0	instant	instant
11	FC-4, 0.5%	HC-2, 0.5%	1.0	1.0	instant	instant
C16	—	HC-2, 0.6%	3.0	1.5	5 min	> 24 hr
C17	—	—	2.0	1.5	instant	instant

The data in TABLE 6 show that, when using an HP 2500CP printer to 20 apply ink to polypropylene microporous film, the dry time for the ink is instantaneous for the films containing FC-4 fluorochemical surfactant, either alone or in combination with HC-2 hydrocarbon surfactant, as compared to the very long dry times noted when HC-2 was used alone as a polymer melt additive.

Also, better image quality resulted with the fluorochemical surfactant-25 containing films. Additionally, it was noted that incorporating higher levels of hydrocarbon surfactant into the polymer in an effort to improve ink performance resulted in poor quality films which were too fragile for the print test.

Examples 12-15 and Comparative Examples C18-C21

The films made for Examples 10-11 and Comparative Examples C16-C17 were evaluated with two other printers: the ENCAD™ NOVAJET 4 and the 5 ENCAD™ NOVAJET PRO. The ENCAD™ NOVAJET PRO printer contained a high surface tension dye-type ink. The quality of ink printing was rated according to Bleed, Uniformity, Surface Dry Time and Total Dry Time. Results from these evaluations are presented in TABLE 7.

10

TABLE 7

Ex.	FC, %	HC, %	Printer	Bleed	Uni-formity	Surf. Dry Tm.	Total Dry Tm.
12	FC-4, 1.2%	—	NOVAJET 4	1.0	2.0	20 min	> 24 hr
13	FC-4, 0.5%	HC-2, 0.5%	NOVAJET 4	1.0	2.0	10 min	> 24 hr
C18	—	HC-2, 0.6%	NOVAJET 4	2.0	4.0	45 min	> 24 hr
C19	—	—	NOVAJET 4	1.0	4.0	> 24 hr	> 24 hr
14	FC-4, 1.2%	—	NOVAJET 4	1.5	1.5	instant	instant
15	FC-4, 0.5%	HC-2, 0.5%	NOVAJET 4	1.5	1.5	instant	instant
C20	—	HC-2, 0.6%	NOVAJET 4	1.5	2.0	3 min	> 24 hr
C21	—	—	NOVAJET 4	1.5	4.0	> 24 hr	> 24 hr

The data in TABLE 7 show that, when ink is applied to the microporous film with the NOVAJET 4 printer, a general improvement in ink bleed, uniformity and surface drying time when a fluorochemical surfactant was employed as a 15 polymer melt additive, either alone or in conjunction with a hydrocarbon surfactant. Using the Novajet Pro printer, a striking reduction in ink drying times was noted when employing a fluorochemical surfactant as a polymer melt additive.

CLAIMS

1. Method of printing a substrate comprising the steps of:
 - providing a substrate selected from the group consisting of (i) a 5 non-woven web comprising fibers of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant and (ii) a microporous film comprising a layer of olefinic thermoplastic polymer having dispersed therein a non-ionic fluorochemical surfactant and;
 - image-wise applying ink to said substrate,
 - 10 and said olefinic thermoplastic polymer being a polymer consisting of repeating units derived from alpha olefins having 2 to 4 carbon atoms.
2. Method according to claim 1 wherein said olefinic thermoplastic polymer is polypropylene.
- 15 3. Method according to claim 1 wherein said non-ionic fluorochemical surfactant corresponds to the following formula:
$$(R_f)_n-Q-(Z)_m \quad (I)$$
wherein:
 - 20 each R_f may be the same or different and represents a fluoroaliphatic group having at least 3 fully-fluorinated carbon atoms;
 - each Q is a multivalent linking group, or is a covalent bond;
 - each Z may be the same or different and represents a nonionic, water-solubilizing group comprising a poly(oxyalkylene) group; and
- 25 n and m independently represent a number from 1 to 6.
4. Method according to claim 1 wherein said non-ionic fluorochemical surfactant corresponds to the following formula:
$$R_f-L-G-X-T \quad (II)$$
- 30 wherein R_f represents a fluoroaliphatic group having at least 3 fully-fluorinated carbon atoms, L is a linking group or a covalent bond, G is a water solubilizing

poly(oxyalkylene) group, X is oxygen or NR with R representing hydrogen or an alkyl or aryl group, and T is hydrogen or an organic group.

5. Method according to claim 4 wherein T represents hydrogen or an
5 organic group having not more than 6 carbon atoms.

6. Method according to claim 1 wherein said ink is a water based ink.

7. Method according to claim 1 wherein said non-ionic fluorochemical
10 surfactant is dispersed in said olefinic thermoplastic polymer in an amount between
0.2% by weight to 6% by weight relative to the total weight of said olefinic
thermoplastic polymer.

8. Method according to claim 1 wherein said layer of olefinic
15 thermoplastic polymer or said olefinic thermoplastic polymer fibers further
comprises a non-ionic non-fluorochemical polyoxyalkylene surfactant.

9. Method according to claim 8 wherein said non-ionic non-
fluorochemical polyoxyalkylene surfactant corresponds to the following formula:

20 $R_h^1-Y^1-W-Y^2-R_h^2$ (III)

wherein:

W represents a polyoxyalkylene group;

Y¹ and Y² independently represent an oxygen or sulfur atom or a group of
the formula -CO-, -COO-, -NH-, -CONH-, or -N(R)- where R is an alkyl group or
25 an aryl group;

R_h^1 represents an alkyl or an aryl group and

R_h^2 represents a hydrogen atom or is an alkyl or an aryl group.

10. Method according to claim 8 wherein the weight ratio of said non-
30 ionic fluorochemical surfactant to said non-ionic non-fluorochemical
polyoxyalkylene surfactant is between 9:1 and 4:6.

11. Method according to claim 1 wherein the image-wise application of ink proceeds via inkjet printing.

12. Microporous film comprising a layer of olefinic thermoplastic 5 polymer having dispersed therein a non-ionic fluorochemical surfactant wherein the olefinic thermoplastic polymer is a polymer consisting of repeating units derived from alpha olefins having 2 to 4 carbon atoms.

13. Microporous film according to claim 12 wherein said olefinic 10 thermoplastic polymer is polypropylene.

14. Microporous film according to claim 12 wherein said non-ionic fluorochemical surfactant corresponds to the following formula:



15. wherein:

each R_f may be the same or different and represents a fluoroaliphatic group having at least 3 fully-fluorinated carbon atoms;

Q is a multivalent linking group, or is a covalent bond;

each Z may be the same or different and represents a nonionic, water-20 solubilizing group comprising a poly(oxyalkylene) group; and
 n and m independently represent a number from 1 to 6.

15. Microporous film according to claim 12 wherein said non-ionic fluorochemical surfactant correspond to the following formula:



wherein R_f represents a fluoroaliphatic group having at least 3 fully-fluorinated carbon atoms, L is a linking group or a covalent bond, G is a water solubilizing poly(oxyalkylene) group, X is oxygen or NR with R representing hydrogen or an alkyl or aryl group, and T is hydrogen or an organic group.

30

16. Microporous film according to claim 15 wherein T represents hydrogen or an organic group having not more than 6 carbon atoms.

17. Microporous film according to claim 12 wherein said non-ionic
fluorochemical surfactant is contained in said layer of olefinic thermoplastic
polymer in an amount between 0.2% by weight to 6% by weight relative to the
5 total weight of said layer of olefinic thermoplastic polymer.

18. Microporous film according to claim 12 printed on at least part of at
least one of its major surfaces with a image pattern of ink.

10 19. Microporous film according to claim 18 wherein said ink is a water
based ink.

15 20. Microporous film according to claim 12 wherein said layer of
olefinic thermoplastic polymer further comprises a non-ionic non-fluorochemical
polyoxyalkylene surfactant.

21. Microporous film according to claim 20 wherein said non-ionic
non-fluorochemical polyoxyalkylene surfactant corresponds to the following
formula:

20 $R_h^1-Y^1-W-Y^2-R_h^2$ (III)

wherein:

W represents a polyoxyalkylene group;

Y¹ and Y² independently represent an oxygen or sulfur atom or a group of
the formula -CO-, -COO-, -NH-, -CONH-, or -N(R)- where R is an alkyl group or
25 an aryl group;

R¹_h represents an alkyl or an aryl group and

R²_h represents a hydrogen atom or is an alkyl or an aryl group.

22. Microporous film according to claim 20 wherein the weight ratio of
30 said non-ionic fluorocelical surfactant to said non-ionic non-fluorochemical
polyoxyalkylene surfactant is between 9:1 and 4:6.

INTERNATIONAL SEARCH REPORT

Int'l. Appl. No.

PCT/US 99/11053

A. CLASSIFICATION OF SUBJECT MATTER	IPC 7 C08J5/18	B41M5/00	D06P5/30	D01F1/10	D01F6/04
	D01F6/06	C08K5/00			

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06P B41M C08J D01F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 44508 A (MINNESOTA MINING & MFG) 27 November 1997 (1997-11-27) page 14, line 23 – line 29; claims & US 5 804 625 A (TEMPERANTE ET AL.) 8 September 1998 (1998-09-08) cited in the application —	12-17, 20-22
X	DATABASE WPI Section Ch, Week 199437 Derwent Publications Ltd., London, GB; Class A14, AN 1994-299912 XP002130391 & JP 06 228359 A (NITTO DENKO CORP), 16 August 1994 (1994-08-16) abstract — —/—	12

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
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Date of the actual completion of the International search

11 February 2000

Date of mailing of the International search report

22/02/2000

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INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 99/11053

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 693 587 A (CANON KK) 24 January 1996 (1996-01-24) the whole document	1
A	US 5 084 340 A (LIGHT WILLIAM A) 28 January 1992 (1992-01-28) the whole document	1-11

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